UNCLASSIFIED

AD NUMBER

AD054128

NEW LIMITATION CHANGE

TO

Approved for public release, distribution
unlimited

FROM

Distribution authorized to U.S. Gov't.
agencies and their contractors; Specific
Authority; 17 Jan 55. Other requests shall
be referred to Naval Research Lab.,
Washington, DC.

AUTHORITY

Naval Research Laboratory, Technical
Library, Research Reports Section Notice,
dtd October 25, 2000.

THIS PAGE IS UNCLASSIFIED

AD 54128

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED

A METALLURGICAL EVALUATION OF REFRACTORY COMPOUNDS FOR CONTAINING MOLTEN TITANIUM

PART III - BORIDES AND SULFIDES

E. J. Chapin and W. H. Friske

Nonferrous Alloys Branch
Metallurgy Division

January 17, 1955

A METALLURGICAL EVALUATION OF REFRACTORY COMPOUNDS

FOR CONTAININC MOLTEN TITANIUM

PART III - BORIDES AND SULFIDES

E. J. Chapin ard H. W. Friske

Nonferrous Alloys Branch
Metallurgy Division

January 17, 1955

Naval Research Laboratory
Washington 25, D. C.

CONTENTS

ABSTRACT

Diborides of Ti, Zr, and Cr in crucible form were investigated for melting titanium. In all cases the molten titanium r e a c t e d with the crucible at the interface to produce general solution attack and to cause severe contamination of the metal with brittle boron compounds. Solution of the reaction products resulted in an increase in melting point, making pouring difficult. These borides are not considered promising as crucible materials.

CeS was also investigated in crucible form. General solution attack of the crucible occurred with contamination of the titanium melt. Metallographic and chemical analytical evidence indicates a binary eutectic system between Ti and CeS. In spite of the appreciable contamination with sulfur the hardness level was increased only moderately. Further investigation is required to determine if larger crucibles would be beneficial in minimizing sulfur pick-up by the molten metal.

PROBLEM STATUS

This report completes the investigation of borides and sulfides as crucible materials for melting titanium. This report concludes this phase of the problem, work on other phases is continuing.

AUTHORIZATION

A METALLURGICAL EVALUATION OF REFRACTORY COMPOUNDS FOR CONTAINING MOLTEN TITANIUM
PART III - BORIDES AND SULFIDES

INTRODUCTION

The essential refractory requirements for melting titanium and the results of the investigation of selected oxides were presented in Part I (1) of this series of reports. The results of the investigation of pure carbon, graphite, and selected carbides were presented in Part II (2). The results of the investigation of borides and sulfides are presented in Part III, the last of this series of reports.

A survey of data on compounds having melting points above 1800°C (Part I, References 1 to 24) included several high melting borides. The limited information on these compounds prevented direct selection of those with the best high-temperature stability which would be useful for crucibles for melting titanium. A consideration of the behavior of boron with the elements of the periodic table, however, revealed that boron did not form intermediate phases with certain elements. Specifically, the transition elements of the fourth, fifth, and sixth groups appeared to form borides having maximum possibilities as stable materials. The borides, like the carbides, also tend to decrease in stability with increasing atomic number within a period; therefore, the most stable borides appeared to be those of Ti, Zr, and Hf with Nb and Ta as second best and those of Cr, Mo, and W as third best. The borides of Ti, Zr, and Cr were selected for investigation, since these were the only compounds available at the time. Crucibles of all three borides were prepared by hot pressing in graphite at about 2000°C, some being obtained from source E and some from Source I (1). The crucible dimensions were about 1 in. o.d. by 11/16 in. i.d. by 2 in. height.

The survey of data on compounds melting above 1800°C revealed a limited number of sulfides with high melting points and apparently good high temperature stability. Two such compounds, CeS and ThS, appeared to have appropriate properties for use as crucible materials. The availability of these materials was highly restricted at the time of selection so that only two crucibles of CeS were obtained for investigation. These measured about 1 in. o.d. by 3/4 in. i.d. by 1-5/8 in. high. The method of their preparation is not known but it is probable that they were fabricated by hydrostatic pressing followed by sintering at about 1950°C in vacuum.

Inasmuch as the experimental details were discussed in Part I, only a brief review of the melting procedure employed in the investigation of the boride and sulfide crucibles is presented. All of the boride crucible melts and those of one CeS crucible were made in a tilting molybdenum furnace fitted with a tungsten wire heater using either high-vacuum or liquid nitrogen-trapped-pure helium. Melts made in a second CeS crucible were made in a high-frequency induction, high-vacuum furnace with solidification of the melt in the crucible. A solid charge of arc-fused titanium was introduced into the hot, outgassed crucible and melted within 3 to 7

minutes from the time of introduction. The melt generally was held 2 to 3 minutes at a superheat of about 25°C before pouring. In some instances a superheat of about 200°C was employed.

INVESTIGATION OF BORIDES

Boron exhibits a peculiar behavior in its binary compounds with metals. It displays a strong tendency to form links with itself in the form of long chains and two or three dimensional structures into which the metallic elements are fitted. The binary metallic borides therefore do not have the simple composition which may be expected from the valencies and usually contain more boron atoms than the valencies require.

As a class, the borides exhibit great chemical inertness, extreme melting points and hardness, and low volatility at elevated temperatures in either vacuum or in a neutral atmosphere. These properties appear to result from the strong bonds between boron atoms forming a boron structure, rather than from forces acting between the boron and the metal atoms.

The borides appear to be more stable than the respective carbides of the same elements as indicated by the facility of conversion of the carbides to borides in the presence of either boron or boron carbide. From a thermal stability standpoint, the diborides of the fourth group metals and the monoborides of the sixth group appear to be the most stable. The fifth group metals form borides which exhibit about equal thermal stability regardless of composition.

The borides having a simple hexagonal structure appear to be isomorphous and may be expected to form a continuous series of solid solutions provided the radius ratios of the metal atoms are favorable. Complete mutual solubility has been reported for the diborides of Ti and Zr. This characteristic introduces serious difficulties for maintaining chemical inertness between a refractory boride and molten titanium. The characteristics of the selected borides are listed in Table 1.

The experimental crucible borides were found to correspond closely to a diboride composition. The results of the analyses are tabulated in Tables 2a and 2b. The observed densities were lower than those reported in the literature for the respective compounds. The low value may have resulted mainly from porosity in the boride bodies as indicated by the difficulty experienced in obtaining a constant weight during density determinations. Carbon was found by chemical analysis to be present in varying amounts in all of the crucible borides with the highest amounts in the source-E, TiB_2 and CrB_2 and in the source-I ZrB_2. Insoluble residues were isolated from the source-E TiB_2 and the source-I TiB_2 and ZrB_2 crucibles. These residues gave an X-ray diffraction pattern identical with that of B_4C. Other carbides, although not detected, may have been present in small amounts. From this evidence it may be assumed that the bulk of the carbon was combined as boron carbide which occurred as a dispersed phase in the crucible borides.

Chemical analysis also showed that the borides contained from about 0.1 to 0.26 wt % oxygen, from 0.012 to 0.25 wt % nitrogen, and from 0.006 to 0.007

2

TABLE 1
Characteristics of Selected Borides

Boride	Density (g/cc)	Melting Point (°C)	Thermal Conductivity (cal/cm sec °C)	Resistivity (michrohm-cm)	Micro-hardness (Kg/mm²)	Other Phases in Metal-Boron System
TiB_2	4.5	2980	0.0624	15.2	3400*	Ti_2B, TiB, Ti_2B_5
ZrB_2	6.1	3040	0.0550	9 – 11	2200*	ZrB, ZrB_{12}
CrB_2	5.6	1850		21	1800†	CrB, Cr_3B_4
CrB	6.2	1550		64		Cr_2B, Cr_3B_2

* 50 g load
† 100 g load

TABLE 2a

X-ray Diffraction Data and Densities of Experimental Boride Crucibles

Crucible Boride	Crucible Source	Lattice Constants (Å) Observed	Lattice Constants (Å) Literature	Compound Identity	Density (g/cc) Observed	Density (g/cc) Literature
TiB_2	E	a_0 3.029 c_0 3.234 c/a 1.067	a_0 3.028 c_0 3.228 c/a 1.064	TiB_2 (hex)	3.98	4.38* 4.52†
TiB_2	I	Identical with TiB_2 (source E)		TiB_2	3.77	
ZrB_2	E	a_0 3.168 c_0 3.538 c/a 1.117 One unidentified weak line	a_0 3.170 c_0 3.533 c/a 1.114	ZrB_2 (hex)	5.34	6.09†
ZrB_2	I	Identical with ZrB_2 (source E)		ZrB_2	4.88	
CrB_2	E	a_0 2.985 c_0 3.081 c/a 1.032	a_0 2.969 c_0 3.066 c/a 1.032	CrB_2 (hex)	4.74	5.6†

*Weight method
†X-ray

4

Chemical Analytical Data on Experimental Boride Crucibles

Crucible Boride	Crucible Source	Metallic Element of Crucible (wt%)	Boron Total* (wt%)	Boron Carbide† (wt%)	Carbon (wt%)	Oxygen (wt%)	Nitrogen (wt%)	Hydrogen (wt%)
TiB_2	E	60.0	36.6	10(approx)	2.99	0.18	0.25	0.0063
TiB_2	I	69.0	29.7	0.1	0.94			
ZrB_2	E	80.3	19.0	none isolated	0.79	0.09	0.012	0.006
ZrB_2	I	72.8	25.8	8.6	1.10			
CrB_2	E	64.6	33.8	none isolated	1.07	0.26	0.19	0.007

*Calculated by difference

†Identified as B_4C by X-ray diffraction

wt % hydrogen. Although these impurities appeared to be relatively low in amount, their presence cannot be ignored in view of the effects of small amounts of such impurities on the quality of titanium. The preparation of boride crucible bodies devoid of impurities that are harmful to titanium may be assumed to be a technologically difficult task.

Experimental results obtained from melts in boride crucibles are listed in Tables 3a and 3b. Titanium was observed to melt quietly in all of the boride crucibles with no evidence of reaction between crucible and melt nor detectable vapor evolution. One exception occurred in the case of a second melt in a source-E CrB_2 crucible. In this instance a reaction occurred between the crucible and the melt resulting in such vigorous bubbling as to cause the molten metal to overflow the crucible. During the course of this reaction a dark film was observed to form on the surface of the molten metal and to separate intermittently exposing bright metal.

All of the borides were wetted by molten titanium demonstrating a high affinity between the molten metal and the respective boride compound. The melts were observed to become viscous soon after the charge became entirely liquid and none of the melts could be completely emptied. A strong tendency was observed for melts to solidify at $1775^{\circ}C$, the melting temperature nominally employed. This behavior was clearly demonstrated in the case of an initial melt in a source-I TiB_2 crucible in which the charge was observed to melt completely and then solidify shortly thereafter at a temperature of about $1775^{\circ}C$. Upon rapidly raising the temperature to almost $2000^{\circ}C$ remelting was observed to progress from the central portion of the solidified charge toward the crucible walls. Only partial remelting was achieved, however, as the melt was observed to resolidify at the higher temperature. Thus, the effect of increasing the temperature to obtain fluidity merely served to increase the reactivity between the crucible and the melt and to accelerate the solution of the products of reaction into the melt. This resulted in an increased melting point which may explain the unsatisfactory pouring characteristics observed in all of the melts made in the boride crucibles.

The introduction of a solid metal charge into a boride crucible heated above $1300^{\circ}C$ always resulted in the metal becoming bonded to the crucible at the point of contact. Once bonding occurred, it was not possible to detach the solid metal. This characteristic demonstrated the high affinity that existed between solid titanium and the respective borides at elevated temperatures and also showed that a reaction between the crucible and the metal was initiated in the solid state. The metal was always preheated prior to contact with the crucible by suspending it inside the crucible but not in contact with it.

The boride crucibles were observed to have good thermal shock resistance and no cracking occurred either during the introduction of the somewhat cooler metal charge into a hot crucible, or during melting or after pouring. One exception occurred in which a source-E CrB_2 crucible cracked while making the initial melt. The crucibles wherein the melts were intentionally permitted to solidify showed some cracking which apparently resulted from differences in contraction between metal and crucible upon cooling.

All of the melts solidified in boride crucibles showed deep meniscuses and an acute angle of contact between crucible and melt indicating pronounced wetting by the titanium. General solution attack of the crucibles occurred in all cases as evidenced by the undercutting of the crucible by the melt at the top of the meniscuses. No extensive penetration of the crucible by the molten metal was observed except in one case. The general conditions existing between the various crucibles and their respective melts are illustrated by Figs. 1A (TiB_2), 1B (ZrB_2), 2A (CrB_2), and 2B (TiB_2). The melt which had been reheated to almost 2000°C and resolidified at that temperature is shown in Fig. 2B. The only instance of vigorous reaction between molten titanium and a boride crucible is shown in Fig. 3A. The melt rapidly became liquid and two attempts to pour it in the first 3 minutes after melting was achieved were unsuccessful. Upon increasing the temperature to about 1850°C from about 1750°C the melt was seen to bubble vigorously and overflow. After the melt had cooled a purplish film was observed on the surface of the metal which when analyzed spectroscopically gave a positive test for elemental chromium. The crucible was severely attacked, particularly along cracks. Reported data (3) on the melting points of several chromium boride phases indicate the possibility of a liquid phase forming at the crucible interface between CrB_2 and molten Ti. The melting points for Cr_3B_2, CrB, and CrB_2 are reported as 1960°C, 1550°C, and 1850°C, all ±50°C. Since a needle phase was found in the melt that closely approached the composition of TiB, it may be inferred that reduction of CrB_2 occurred to CrB with vaporization of reduced chromium and gradual melting of the crucible walls. The large cavities occurring in this melt indicate decomposition of the boride and release of chromium vapor.

Examination of the interfacial conditions existing between the melts and the crucibles was hampered by the separation of the melts from the crucible upon cooling. The metal side of the interface of a melt made in a source-E TiB_2 crucible is shown in Fig. 3B. In this case a needle-like phase formed at the interface which was probably of intermediate boron content and quite soluble in the melt. In the case of a source-I TiB_2 crucible which had been heated to almost 2000°C the effect of temperature on the reactivity of the crucible and the melt at the interface is illustrated by Fig. 4A. In this case the attack of the crucible boride was more extensive and resulted in an altered zone in the crucible and a heavy concentration of the needle phase in the metallic matrix.

In the case of melts made in source-E ZrB_2 crucibles the interfacial conditions are shown by Fig. 4B. The reaction zone between the crucible and the melt appeared well defined with a continuous transition across the interface. The attack of the boride by the melt appears to occur at the boride grain boundaries and alteration of the boride proceeds with the formation of a needle-like phase which has some solubility in the melt. Melts made in source-E CrB_2 crucibles showed similar interfacial conditions, as illustrated by Fig. 5A. The crucible boride was attacked by the molten metal and the needle-like phase is shown clearly at the crucible interface and in the metallic matrix. There is a striking similarity in shading and color between the phase at the interface and the detached needles in the melt indicating the probability of both having a like composition. The sharply outlined particles in the melt are believed to be carbides. Upon etching the sample of Fig. 5A,

7

TABLE 3a
Experimental Melting Data for Boride Crucibles

Melt No.*	Crucible Boride	Crucible Source	Outgas Temp. (°C)	Charge** (grams)	Min. to Melt Down	Min. Held Molten	Super-Heat (°C)	Atmosphere†	Pourability††
RM-26-1	ZrB_2	E	1800	13.0 (I)	107	3	125	Vac	3
2			1750	18.0	5	2	50	Vac	2.3
3				16.5	7	2	25	Vac	2.3
4				17.5	3.5	1	25	Vac	2
RM-29-1	ZrB_2	I	1800	11.5	75	3	25	Vac	2.3
2				11.5	7	8	200	Vac	2.3
3				6.5	85	6	75	He	4
RM-47	ZrB_2	E	1800	20.0	58	4	25	Vac	5
RM-31-1	TiB_2	E	1800	17.0	106	1.5	25	He	2.3
2				20.0	82	2.0	200	He	4
RM-35-1	TiB_2	I	1825	17.5	31	2.0	25	He	4
2				remelt	140	5.0	200	He	4
RM-48	TiB_2	E	1850	16.0	72	2.0	25	Vac	5
RM-32-1	CrB_2	E	1800	18.0	17	2.0	25	He	2
2				21.0	85	5.0	50	He	4
RM-45	CrB_2	E	1850	20.0	96	3	25	Vac	5
RM-52-1	CrB_2	E	1850	20.0	84	2	25	Vac	2
2				20.0	83	3	25	Vac	2
3				20.0	43	2	25	Vac	2

*Designates crucible and order of consecutive melts
**Arc-fused sponge Ti, except where (I) designates iodide quality Ti
†Vac = high vacuum; He = liquid-nitrogen-trapped helium
††1 = poured completely; 2 = residual metal frozen on crucible lip; 3 = residual metal frozen in crucible; 4 = would not pour; and 5 = intentionally solidified in crucible

TABLE 3b

Chemical Analytical Data and Hardnesses of Melts Made in Boride Crucibles

Melt No.*	Crucible Boride	Crucible Source	Carbon (wt %)	Insoluble Residue in HCl (wt %)	Boron (wt %)	Chromium (wt %)	Oxygen (wt %)	Phases in Micro-structure‡	Hardness (DPH) As Cast	Hardness (DPH) Solidified in Crucible
RM-26-1 2,3,4**	ZrB$_2$	E	0.16 0.16	none none	-- 5.8	-- --	0.017 0.75	A,B A,B	278 572	
RM-29-1 2	ZrB$_2$	I	0.29 0.55	none none	-- 4.9	-- --	0.093 0.21	A,B A,B	341 536	223
RM-47	ZrB$_2$	E	0.32	none	2.6	--		A,B,C		
RM-31-1 2	TiB$_2$	E	0.26 0.44	0.90† ††	-- 14.9	-- --	0.150	A,B A,B,C	277 325# 1300§	
RM-35-2	TiB$_2$	I	0.14	20.9††	11.4	--	0.102	A,B,C		410#§ 1400§¶
RM-32-1	CrB$_2$	E	0.41	3.05†	2.07	3.99	0.083	A,B	497	
RM-45	CrB$_2$	E	0.57	--	1.97 (cal)	3.81		A,B,C		275
RM-52-1 2 3	CrB$_2$	E	0.13 0.28 0.19	-- -- --	1.01 (cal) 1.56 (cal) 1.68 (cal)	1.92 2.98 3.22	0.079 0.113 0.083	A,B A,B A,B	297 297 283	

*Designates crucible and order of consecutive melts
**All three melts poured into one ingot
†Identified as TiC by X-ray diffraction
††Large TiB needles isolated and identified by X-ray diffraction
‡A = basket weave matrix; B = boride needles; and C = carbides
#Metal matrix
§Needle phase
¶Froze in crucible

Fig. 1A - Solidified melt in TiB_2 crucible; 2X, melt no. RM-48

Fig. 1B - Solidified melt in ZrB_2 crucible; 2X, melt no. RM-47

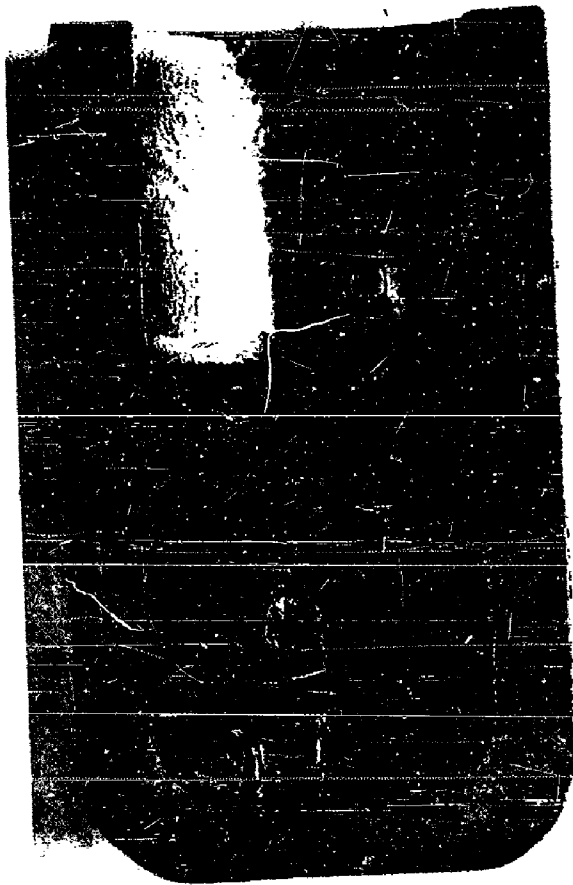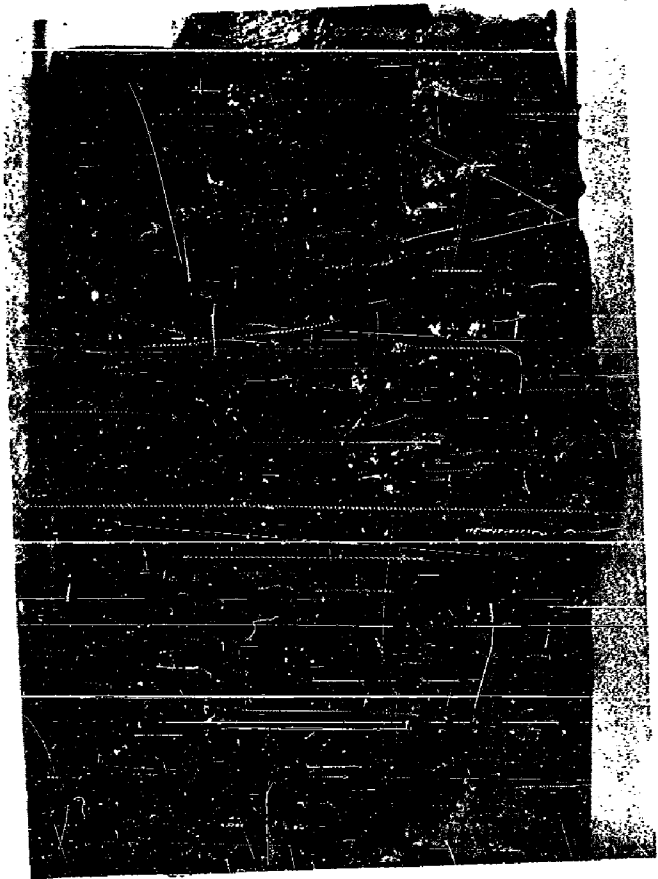Fig. 2A - Solidified melt in CrB_2 crucible; 2X, melt no. RM-45

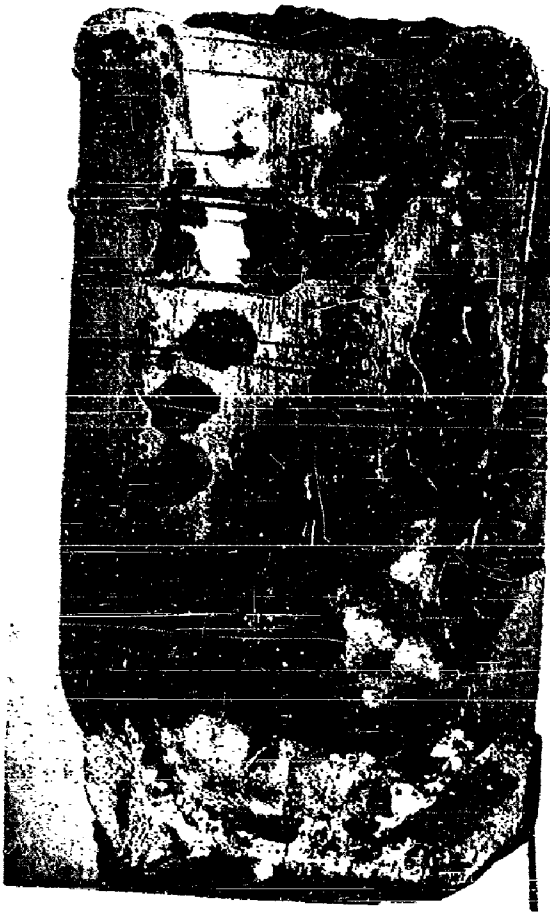Fig. 2B - Remelt in TiB_2 crucible solidified after reaching approximately 2000C; melt no. RM-35-2.

Fig. 3A - Example of vigorous reaction between molten Ti and CrB_2 crucible; 2X, melt no. RM-32-2

Fig. 3B - Metal side of interface showing development of needle phase; 500 X, unetched, melt no. RM-48

Fig. 4A - Interface conditions in TiB$_2$ crucible in which mcl solidified at about 2000°C; 100X, melt no. RM-35

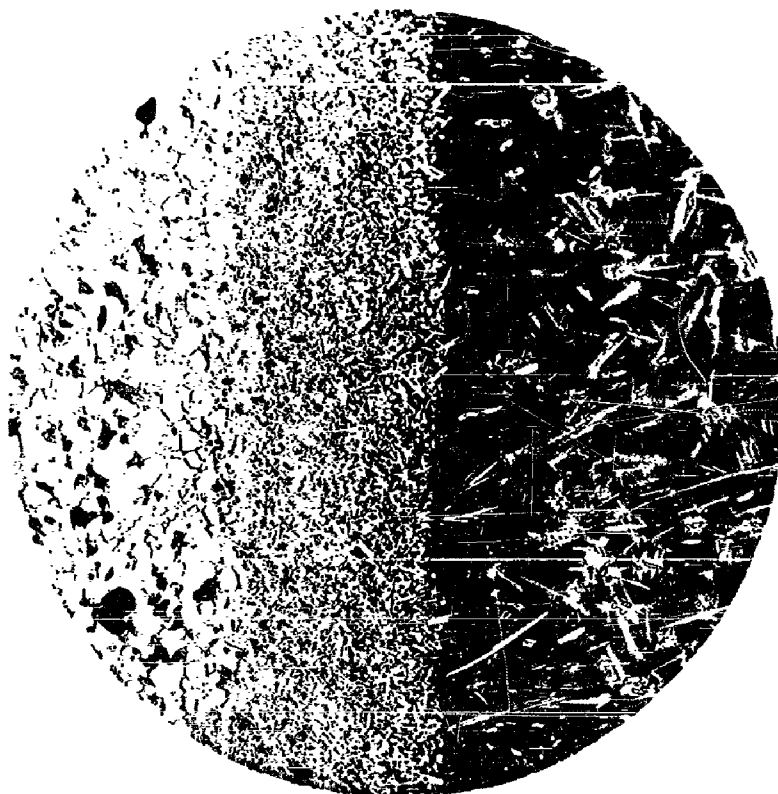Fig. 4B - Interface conditions existing between melt and ZrB$_2$ crucible; 100X, melt no. RM-47

13

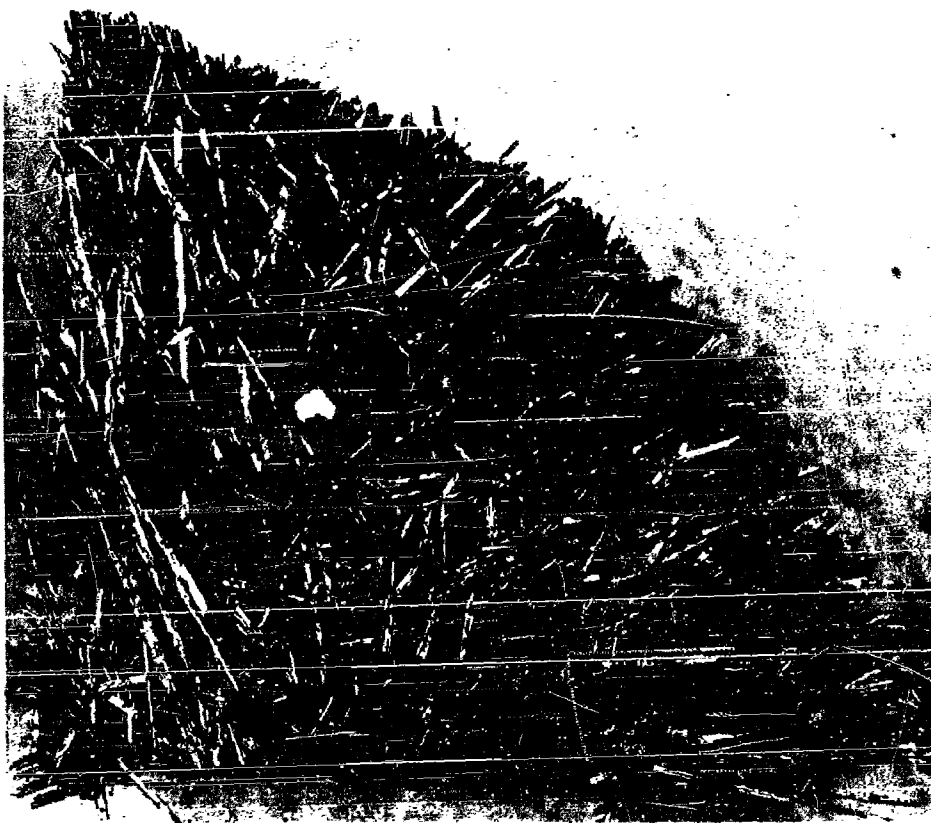Fig. 5A - Interface conditions existing between melt and CrB_2 crucible; 500X, unetched, melt no. RM-45

Fig. 5B - TiB needles in their original location within the sample from a melt in a TiB_2 crucible; 15X, melt no. RM-35

the phase occurring at the interface presented sharp boundaries adjacent to the melt but remained unchanged adjacent to the crucible. The needles in the metallic matrix were likewise outlined sharply after etching.

The interfacial phase dissolved in the melt generally separated upon solidification as distinct needles or platelets, the abundance or size of which appeared to be dependent largely upon the melting temperature and the rate of cooling of the melt. Slow cooling appeared to promote their growth into coarser dimensions as was noted in the cases where melts were solidified in the crucibles. Chill cast metal contained needles of very small size.

Solution treatment of samples of melts made in TiB_2 crucibles, with HCl permitted chemical separation of the needle-like phase found in the microstructures. The abundance and distribution of the needle phase in the metallic matrix is illustrated by Fig. 5B, which represents an advanced stage of acid dissolution. The needles are in their original location within the sample. Single needles, analyzed spectrochemically and by X-ray diffraction, were found to be a pure compound of titanium and boron containing 82.3 wt % Ti, and having an orthorhombic structure with lattice constants $a_0 = 6.16Å$, $b_0 = 3.06Å$, and $c_0 = 4.59Å$. These values are in good agreement with those reported for the compound TiB (4) and it may be concluded from this evidence that titanium diboride reduces to the monoboride when placed in contact with molten titanium. Needles occurring in the melts made in either ZrB_2 or CrB_2 crucibles could not be isolated by this method. It was possible, however, to separate enough needles mechanically from melts made in the ZrB_2 and the CrB_2 crucibles to obtain X-ray patterns. The major lines obtained with needles from a ZrB_2 melt were nearly identical with those for TiB, while the needles from a CrB_2 melt contained a number of spotty unidentified lines in addition to those of TiB. The fact that TiB was identified in all of the melts irrespective of the boride composition of the crucible strongly indicates that titanium is a stronger boride former than either Zr or Cr. From this evidence it appears unlikely that titanium could be melted in any known diboride without the melt becoming contaminated with needles composed of Ti, B, and a third element derived from the crucible boride.

Solution treatment of the samples of the melts in some cases yielded additional small amounts of insoluble residues which were found by X-ray diffraction to be principally TiC. Chemical analyses (Table 2B) revealed that all of the crucible borides contained varying amounts of carbon which in some cases occurred as B_4C; in other cases the carbon could not be isolated in any form. The presence of carbides in the microstructures, as in Fig. 5A, leads to the conclusion that TiC may be formed during melting and that this phase may co-exist with a boride phase in the melt.

The microstructures of the melts made in crucibles of the borides of Ti, Zr, and Cr showed certain similar characteristics. The metallic matrix was generally of a basket weave pattern and the boride phase contained therein was needle-like or in platelets. The microstructure of Fig. 6A represents a melt poured from a TiB_2 crucible, Fig. 6B represents that from a ZrB_2 crucible, and Fig. 7A represents that from a CrB_2 crucible. The interface conditions between molten titanium contaminated with reaction products

15

Fig. 6A - Platelets of boron compound, TiB, in melt cast from TiB_2 crucible; 500X, unetched melt no. RM-31-1
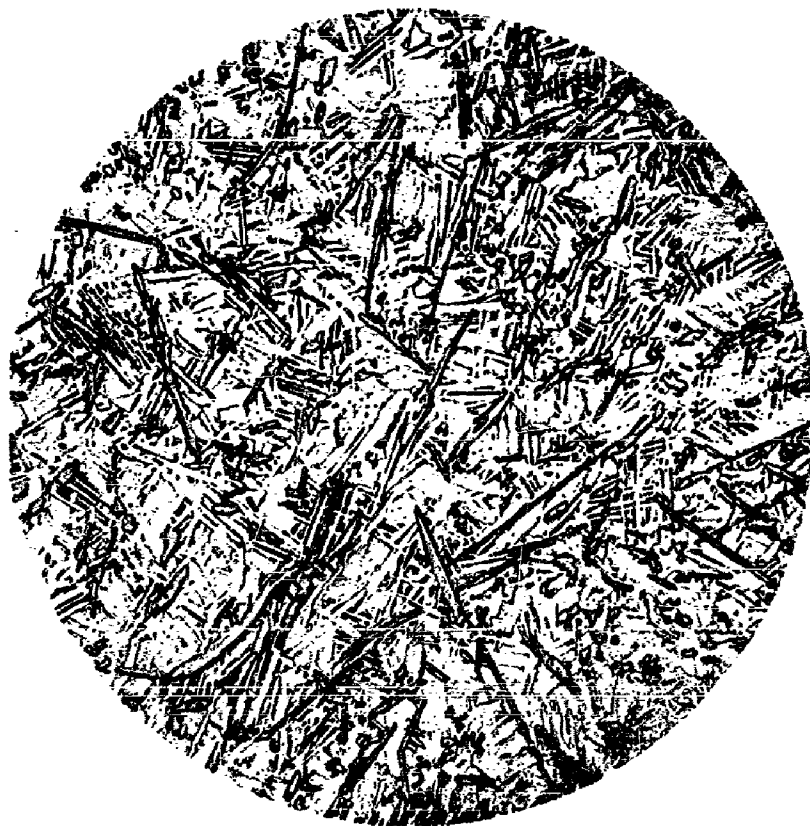

Fig. 6B - Needles of a boron compound in melt cast from ZrB_2 crucible; 500X, etched, melt no. RM-29-1

from contact with a CrB_2 crucible and the solid <u>unmelted</u> charge is shown in Fig. 7B. It is apparent from this microphotograph that boron diffusion proceeded rapidly in the solid titanium, developing a basket weave pattern in advance of melting. The metallic phase of the microstructures was not investigated in detail; however, it is believed that in the cases of ZrB_2 and CrB_2 crucibles, ternary solid solutions and boride phases were formed. The boride phases are believed to be composed of solutions of TiB in a lower crucible boride. This deduction is based on the ability to separate chemically a pure binary boride (TiB) from melts made in TiB_2 crucibles, whereas in the melts made in the ZrB_2 and CrB_2 crucibles such chemical separation was not obtained. This indicated that chemical instability is promoted in those boride phases which deviate from binary compositions.

It was difficult to obtain a representative hardness average for the individual melts. The boride phases were exceedingly hard and brittle, and measured about 1600 DPH while the hardness of the metallic matrices varied from 275 to over 500 DPH. In general, the hardness level was considerably above that considered optimum for good metal quality. The brittle character of the boride phases is a factor seriously detrimental to metal properties.

It is concluded that in spite of their apparent excellent high-temperature properties, the borides lack the necessary chemical inertness toward molten titanium and therefore cannot be recommended as suitable crucible materials.

INVESTIGATION OF CERIUM SULFIDE

A number of stable metallic sulfides such as the mono-sulfides of cerium, thorium, uranium, and others have been discussed by Brewer et al. (5) and by Pauling (6). The stability of these compounds is evidenced by their low volatility, high heat of sublimation, and high negative free energy of formation. They cannot be heated in the presence of oxygen, however, since they suffer rapid oxidation and deterioration. The sulfides of rare earth metals, prepared dry and strongly heated in a non-oxidizing atmosphere, resist hydrolysis although boiling water attacks them.

It was reported (7) that CeS crucibles were satisfactory for metals melting below 1800°C while ThS crucibles were satisfactory for those metals melting above 1900°C provided the metals did not form intermetallic compounds with either Ce or Th, which were stable enough to disproportionate either CeS or ThS to a lower sulfide. Except for platinum which disproportionates CeS, no metal was known which would cause serious attack on a CeS crucible. Above 1900°C CeS was reported to develop sufficient vapor pressure to cause evaporation, resulting in surface roughening. The presence of an oxygen impurity in the CeS also produced surface roughening by evaporation of ceric monoxide according to the reaction $Ce_2SO_2 + 3 CeS = Ce_3S_4 + CeO$ (gas). Since nonvolatility is a requirement for chemical stability, it follows that the use of CeS is limited both as to temperature and to amounts of contained oxygen impurities. Prolonged heating of CeS above 1850°C reportedly also produced roughened surfaces as a result of recrystallization.

In the presence of oxygen CeS forms oxysulfides which lower the refractory properties of CeS; if lower sulfides are also present, a eutectic

17

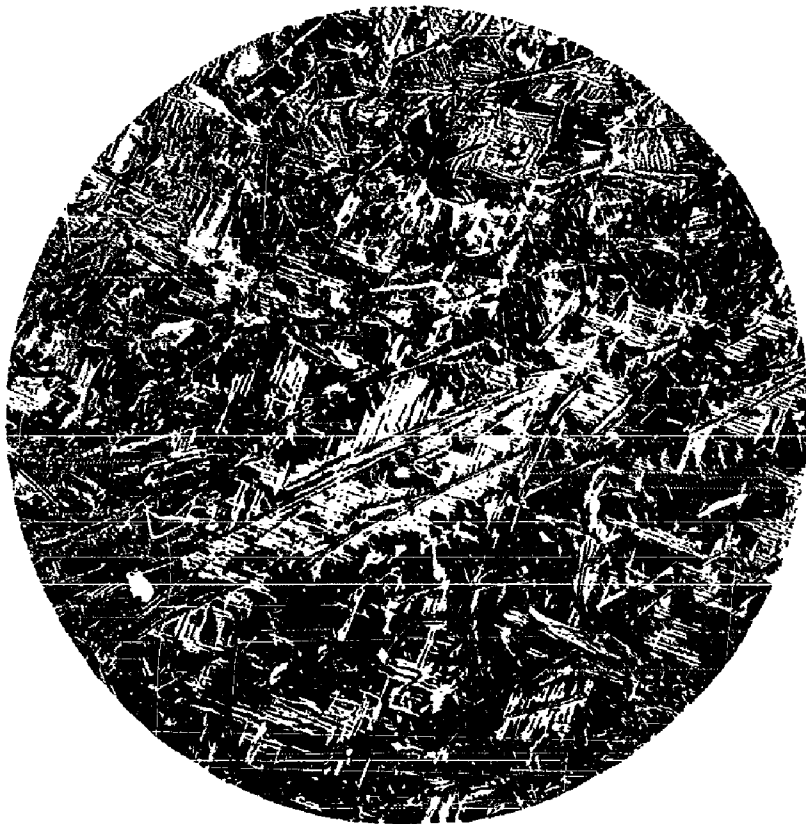Fig. 7A - Needles of a boron compound and structure of metallic matrix of melt cast from a CrB_2 crucible; 250X, etched, melt no. RM-52-1

Fig. 7B - Interface between <u>unmelted</u> Ti charge and melt containing contamination from interaction with CrB_2 crucible; shows development of basket weave pattern in solid metal in advance of melting; 250X, etched, polarized light, melt no. RM-52-2.

$(Ce_2SO_2 - Ce_3S_4)$ which melts at $1650^\circ C$, is formed. With more than 5 wt % of both oxide and lower sulfide impurities, softening occurs above $1750^\circ C$ causing slumping of the material. ThS was stated to be less susceptible to the effects of these impurities.

CeS crucibles were reported (5) to be thermally insensitive and heating rates were reported as high as $1000^\circ C$ per minute without fracture or spalling occurring. Experimental fusions were reported (7) for titanium in CeS crucibles but other than the statement that a sound ingot was obtained without attack on the crucible (although the ingot adhered to the crucible) no details of metal quality were given.

Some of the characteristics which are pertinent to the thermal stability of cerium sulfides are given in Table 4.

A chemical analysis of the CeS crucibles showed a sulfur content of 19 wt %, an amount in slight excess over the required stoichiometric amount of 18.6 wt %. Impurities found spectrographically were Si, Mn, Mg, Fe, Al, and Ca, in order of intensity.

The experimental results of melting titanium in CeS crucibles are listed in Table 5. A 20-gram charge was melted and permitted to solidify in one of the crucibles by using induction heating and high vacuum. After examination of this melt an additional 10-gram charge was added and a second melting was obtained which also was solidified in the crucible. Melting occurred quietly in both cases without evidence of any reaction, although a decidedly yellow colored vapor stream was observed in the high-frequency field issuing from the sight hole in the furnace assembly. The resulting ingot, strongly yellow colored on the surface, adhered to the crucible and could not be removed.

The interface conditions existing between the crucible and the melt are shown by Fig. 8A. An intimate contact between the metal and the crucible was observed. The metal penetrated the crucible apparently along the numerous pores visible in the microstructure. Corrosion of the crucible appeared to proceed by solution attack with complete absence of any intermediate zone at the interface. In an unetched condition the metal contained a black phase and a yellow phase distributed at random throughout the microstructure and a white phase which surrounded some of the solidification grains, forming a eutectic pattern. This melt showed an average Vickers hardness of 280 DPH reflecting an appreciable contamination of the melt.

Nineteen melts were made in the second crucible using resistance heating, either high vacuum or a liquid nitrogen-trapped-helium, and both arc-fused sponge and iodide quality titanium charge material. The crucible finally failed from progressive thinning of its walls resulting from general solution attack as illustrated by Fig. 8B. As in the case of the first crucible, melting occurred without evidence of vigorous reaction or extensive gaseous evolution. The solid metal charge introduced into the hot crucible was observed to stick to it upon the slightest contact and considerable care had to be taken to prevent this from occurring

TABLE 4

Characteristics of Cerium Sulfides

Formula	Density (g/cc)	ΔF_{298} (Kcal)	ΔH_{298} (Kcal)	Melting Point (°C)	Vapor Pressure (microns)	Color	Crystal Habit
CeS	5.93	-117.9	-133.4	2450	1 (at 1900°C)	brass	NaCl
$\frac{1}{4}$ Ce$_3$S$_4$	5.3	-140.4	-120.9	2050	1 (at 1840°C)	black	cubic
$\frac{1}{3}$ Ce$_2$S$_3$	5.2		-115.7	1890	loses sulfur upon heating	red	cubic

TABLE 5
Experimental Melting Data for CeS Crucibles

Melt No.*	Charge** (grams)	Min. to Melt Down	Min. Held Molten	Super Heat (°C)	Atmosphere†	Pourability††	Remarks
RM-36-1	20	13	1.5	25	He	1	
2	22	85	1.5	25	He	1	
3	21	96	1.5	25	He	..	Solid charge stuck to crucible upon introduction
4	23	84	5	50	He	..,3	
5	24 (I)	92	5.5	125	He	4	Residual metal was machined out of crucible
6	7	62	1.5	25	Vac	1	
7	10	67	1.0	25	Vac	2	
8	11 (I)	74	1.5	25	Vac	2	Residual metal was machined out of crucible
9	11½ (I)	83	1.5	25	Vac	1	
10	11 (I)	61	10.5	50	Vac	2	
11	15 (I)	120	3.5	50	He	2,3	Melted under helium, poured in vacuum
12	8	62	1.0	25	Vac	2	
13	11	78	1.0	25	Vac	3	
14	12	63	1.0	25	Vac	3	
15	10	63	1.0	25	Vac	1	
16	14	31	1.5	25	Vac	1	
17	15	59	2.0	10	Vac	4	Unable to super heat, heater failed
18	3	120	6.0	100	Vac	1	Remelt of RM-36-17
19	11	19	1.0	25	Vac	2	Crucible failed
RM-4A	20 (P)	210	5.0	>200	Vac	5	Crucible heated by high-frequency induction
4B	4	360	3.0	>200	Vac	5	Remelt of RM-4A; crucible heated by high-frequency induction

*Designates crucible and number of repeated melts

**Arc-fused sponge Ti, except where (I) designates iodide quality Ti and (P) designates BuMines Ti powder

†He = liquid-nitrogen-trapped helium; Vac = high vacuum

††1 = poured completely; 2 = residual metal frozen on crucible lip; 3 = viscous, poured sluggish; 4 = would not pour; 5 = intentionally solidified in crucible

Fig. 8A - Interface conditions existing between melt and CeS crucible; note absence of reaction zone at the interface; 100X, etched

Fig. 8B - CeS crucible condition after 19 melts had been cast; failure occurred from progressive solution of walls; 2X

near the mouth of the crucibles. This behavior demonstrated the high surface reactivity between the crucible and the metal at elevated temperatures. Where sticking of the charge had occurred near the top of the crucible it became necessary to heat the crucible well above the melting point of titanium to release the charge. Generally, melts made under this difficulty became sluggish and were difficult to pour. A loss of fluidity was also noted when the melt was held for prolonged periods. An increased temperature was required to restore the melt to a liquid condition and a further increase in temperature was required to pour it. Thus, it was necessary to keep the melting temperature and the holding time while molten to a bare minimum in order to minimize the reaction between the crucible and molten titanium. With these precautions, melting and pouring proceeded satisfactorily.

All of the ingots obtained from the melting experiments were coated on the top surface with a bright yellow film. The film could not be identified when compared with known titanium or cerium sulfur compounds, nor did its X-ray diffraction pattern compare with the crucible material. When treated with dilute acid, the film dissolved instantly, producing an odor of H_2S, showing it to be a sulfur compound.

Metallographic studies and chemical analyses, Table 6, indicate that titanium and CeS form a binary eutectic system with the eutectic composition at about 0.4 wt % S (as CeS). In metal that contained less than about 0.4 wt % S the microstructures generally contained alpha titanium grains and some eutectic around the original beta grains. In metal containing more than 0.4 wt % S the microstructure contained a yellow sulfide phase in addition to the eutectic. An example of the hypoeutectic structure is illustrated by Fig. 9A which represents a cast melt containing about 0.165 wt % S. The eutectic is clearly developed in metal containing 0.33 wt % S as illustrated by Fig. 9B. The hypereutectic condition is shown by Fig. 10 in which the metal analyzed 0.96 wt % S. The yellow sulfide phase in this case solidified in dendritic fashion. Holding a melt for prolonged periods seemed to increase the amount of the yellow phase indicating that increased solution of the crucible occurred with time.

The metal cast from the final eight melts was consolidated by arc fusion into a single 70-gram ingot. The microstructure was similar to that of Fig. 10. The ingot was hot forged at 750°C, cold rolled, and swaged. The primary sulfides appeared to have been broken up and dispersed by the mechanical working. For purposes of comparison a 70-gram ingot of selected titanium sponge was prepared by arc fusion and mechanically worked under the same conditions as the ingot consolidated from the melts cast from the CeS crucible.

Hardness studies indicated that metal cast from CeS crucibles was not extensively hardened by the presence of CeS contamination. Melts which analyzed 0.165%, 0.23%, 0.30%, and 0.57% S showed corresponding hardness averages of 185, 192, 201, and 213 DPH, respectively. In comparison, unalloyed arc-fused sponge titanium had an average hardness of 178 DPH while that of iodide quality titanium was about 78 DPH.

TABLE 6
Chemical Analytical Data and Hardness of Melts Made in CeS Crucibles

Melt No.*	Sulfur (wt %)	Cerium (wt %)	Oxygen (wt %)	Phases in Micro-structure††	As Cast Hardness (DPH)
RM-36-1	0.165	0.67	0.074	A,B	185
2	0.23	1.06†	0.091	A,B	192
3	0.3 (approx)	--	0.091	A,B	201, 179‡,200‡‡
4	0.57	2.49†	0.114	B,C	213
5	0.96	4.2†	0.116	B,C	196§
6	0.64	--	--	B,C	160
7	0.34	--	--	B	164
8	0.25	--	--	A,B	118
9	0.33	--	--	A,B	110
10	0.48	--	--	B,C	129
20**	0.61	1.84	0.100	B,C	177, 176#
RM-4A 4B	--	--	--	B,C	280##

*Designates crucible and order of consecutive melts
**Composite ingot of 8 melts (RM-36-12 to RM-36-19), arc-fused in helium and forged at 750°C into a bar
†Calculated by difference
††A = Ti plus eutectic; B = Ti plus eutectic with free cerium at grain boundaries; and C = Ti plus eutectic plus yellow sulfide phase
‡Annealed in vacuum at 1000°C furnace cooled
‡‡Oil quenched from 1000°C in vacuum
§Froze in crucible
#Forged at 750°C
##Intentionally solidified in crucible

Fig. 9A - Example of hypoeutectic structure of cast metal containing 0.165 wt % S from CeS crucible; 500X, etched.
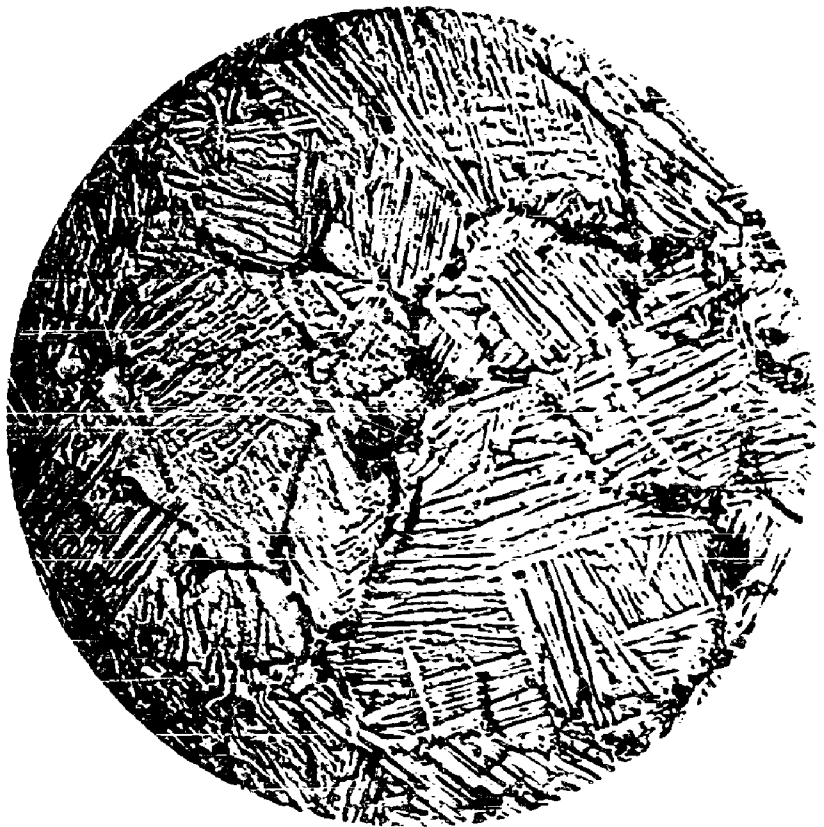

Fig. 9B - Example of eutectic structure of cast metal containing 0.33 wt % S from CeS crucible; 500X, etched, polarized light.
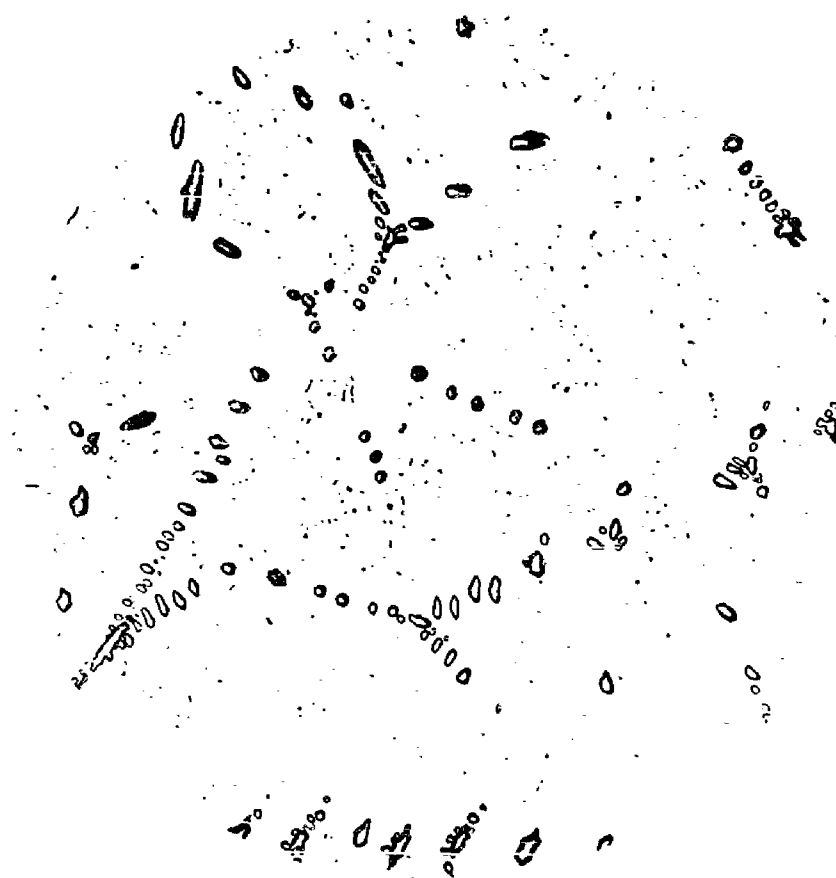
Fig. 10 - Example of hyper eutectic structure
of cast metal containing 0.96 wt % S; 500X,
unetched.

From the material that had been forged at 750°C to 1/4-in. diameter bars, one half was further reduced by rolling and swaging to 0.22-in. diameter and the other half was reduced in flat rolls at 700°C to thin strips. The round stock was machined to three 1/8-in. diameter tensile specimens, while one standard strip tensile specimen was obtained from the flat stock. The tensile properties determined from these specimens are listed in Table 7.

Metal cast from CeS crucibles showed an increase in tensile strength of about 10,000 psi over that of unalloyed sponge titanium (from about 62,000 to 72,000 psi) while ductility as indicated by elongation was lowered from about 40% to 18% for round specimens and from about 32% to 16% for the strip specimens. The hardness of the CeS bearing titanium remained unchanged from its as cast hardness of 176 DPH, while the hardness of the unalloyed sponge titanium was reduced from 166 DPH in the as cast condition to 144 DPH in the final test specimen condition.

Additional mechanical working experiments were conducted on a section of the ingot from the third melt which was reduced by cold swaging from 0.150 in. to 0.048-in. diameter without intermediate annealing. Although reduction was arbitrarily stopped at this point, it apparently could have been continued to a smaller diameter without difficulty. Similarly, a section of an ingot composed of an alloy of iodide titanium and 1 wt % CeS was reduced from 0.150 in. to 0.016-in. diameter by cold swaging without difficulty.

Appreciable amounts of sulfur and cerium were introduced into the metal as a result of solution attack of the crucible by the molten metal. The resulting contamination occurred as a eutectic and as a primary sulfide phase; the amount apparently depended upon melting temperature and holding time while molten. The crucible material appeared to have limitations which did not permit much latitude in temperature for melting titanium. Prolonged contact of the CeS with molten titanium increased the corrosion of the crucible and caused the melt to become viscous and difficult to pour. Increasing the temperature to promote fluidity increased the rate of solution attack by the molten metal and caused accelerated corrosion of the crucible. In spite of the contamination introduced into the metal, the quality of the metal as measured by hardness and mechanical strength was affected only moderately. The presence of cerium and sulfur in titanium increased its strength but decreased its ductility. Compared with the other crucible materials examined, CeS appeared to have the least detrimental effect on the quality of titanium melts.

It cannot be predicted from this investigation if large crucibles could be made satisfactorily from CeS, nor if the larger size crucibles would have the satisfactory shock resistance or the same chemical stability. A larger cross section of molten metal would be advantageous for possibly reducing the amount of contamination. In view of the susceptibility of CeS to attack by oxygen, commercial application of this crucible material would have to definitely exclude oxygen and water vapor from the furnace atmospheres during the melting process.

SUMMARY

The diborides of Ti, Zr, and Cr, in the form of small crucibles, were investigated to determine their suitability for melting titanium. In all cases

TABLE 7

Comparison of Tensile Properties of Titanium Melted in CeS Crucibles
with those of Arc-Fused Unalloyed Titanium

Material	Test Specimen Type	Ultimate Tensile Strength (psi)	Yield Strength 0.2% Offset (psi)	Elongation (%)	Reduction in Area (%)	Hardness (DPH)
RM-36-20*	1/8" dia.	74,700	42,400	15	19	176 (177†)
	1/8" dia.	71,600	47,300	20	29	
AFS**	1/8" dia.	62,200	42,400	39	68	144 '166†
	1/8" dia.	61,500	40,000	47	68	
RM-36-20*	strip (0.036")	72,700	60,600	16	--	
AFS**	strip (0.030")	59,800	45,900	32	--	

*Composite ingot of 8 melts (RM-36-12 to RM-36-19), arc-fused in helium and forged at 750°C into a bar

**Unalloyed sponge Ti arc-fused and forged at 750°C into a bar

†As cast

the molten metal reacted quietly with the crucible at the interface, resulting in the formation of intermediate phases, general solution attack, and serious contamination of the melt with boron and boron compounds. Solution of the reaction products into the melt raised the melting point, making the melts viscous and difficult to pour. An attempt to remelt a frozen charge in a TiB_2 crucible by raising the temperature to almost 2000°C only served to increase the reactivity and resulted in an accelerated solution of reaction products and re-freezing at the higher temperature. Subsequent melts made in the same crucible did not improve in quality but tended to show amounts of contamination about equal to that in the initial melt.

All of the melts showed a characteristic development of a needle-like phase. Melts made in TiB_2 crucibles yielded large needles when samples were solution-treated in HCl. This needle-like phase was identified as TiB. Similar needle-like phases observed in melts from ZrB_2 and CrB_2 could not be isolated by acid treatment but were isolated mechanically from shrinkage cavities. In view of the poor chemical resistance of the phases occurring in melts from ZrB_2 and CrB_2 crucibles, it is concluded that these were not pure binary compounds but probably ternary alloys produced at the crucible-metal interface.

The finely divided portion of the insoluble residue obtained upon solution treatment of metal samples with HCl was identified in some cases as TiC, whereas similar residues isolated from solution treatment of the crucible borides were identified as B_4C. This indicates that titanium can reduce B_4C to form TiC and probably a boride of titanium.

The contamination of the melt with varying amounts of boron compounds resulted in hardnesses ranging from about 275 to over 500 DPH for the metallic matrices. The needles had a hardness of about 1600 DPH, displaying severe brittleness under the indenter.

The borides do not appear to be promising compounds as crucible materials for melting titanium because the borides of Ti, Zr, and Cr, which were considered to offer the most promise, displayed inadequate resistance to solution. Metal quality was drastically affected by the serious contamination of the metal with brittle needle-like phases resulting from the interaction of the crucible boride and molten titanium. The presence of the brittle phases is considered to preclude the development of desirable mechanical properties for metal melted in boride crucibles.

Cerium sulfide (CeS) was investigated in crucible form. Melting proceeded quietly but the presence of a yellow film on metal either chill cast or solidified in the crucible indicated a dissociation tendency for CeS at the melting temperature of Ti. The molten metal appeared to pour without undue difficulty, provided it was not superheated excessively and was not held for prolonged periods: otherwise, it became viscous and difficult to pour.

Metallographic and chemical analytical evidence suggests that titanium forms a binary eutectic system with CeS, with the eutectic composition at about 0.4 wt % S (as CeS). All of the metal melted in CeS crucibles was

29

found to contain appreciable amounts of sulfur ranging from 0.165 to 0.570 wt % with corresponding hardnesses ranging from 185 to 213, respectively. (In comparison, arc-fused titanium of commercial grade and of iodide quality had hardnesses of 178 and 78 DPH, respectively.) Although appreciable amounts of sulfur and cerium were introduced into the metal as a result of solution attack of the crucible, the hardness of the metal was not markedly increased.

The tensile strength of titanium melted in CeS crucibles increased about 10,000 psi over that of the unalloyed commercial grade, while the elongation dropped approximately from 40% to 18%.

CeS is not sufficiently inert to prevent gradual consumption of the crucible by direct solution into the molten metal, but, this material appeared to have the least deleterious effects on the quality of metal melted in any of the materials evaluated in crucible form. Further investigation would be required to determine if larger crucibles would be beneficial in minimizing the contamination observed with small crucibles.

* * *

REFERENCES

1. Chapin, E. J. and Friske, W. H., "A Metallurgical Evaluation of Refractory Compounds for Containing Molten Titanium, Part I - Oxides," NRL 4447, 18 November 1954

2. Chapin, E. J. and Friske, W. H., "A Metallurgical Evaluation of Refractory Compounds for Containing Molten Titanium, Part II - Carbon, Graphite, and Carbides," NRL 4467, 15 December 1954

3. Schwarzkopf, P. and Kieffer, R., "Refractory Hard Metals," p. 299, New York: Macmillan Co., 1953

4. Decker, B. F. and Kasper, J. S., Acta Cryst. 7:77, 1954

5. Eastman, E. D., Brewer, L., Bromley, L. A., Gilles, P. W., and Lofgren, N. L., J. Amer. Chem. Soc., 72:2248, 1950; 72:4019, 1950

6. Pauling, L., "General Chemistry," San Francisco: W. H. Freeman, 1947

7. Eastman, E. D., Brewer, L., Bromley, L. A., Gilles, P. W., and Lofgren, N. L., J. Amer. Ceram. Soc. 34(No. 4):128, April 1951

* * *

Naval Research Laboratory
Technical Library
Research Reports Section

DATE: October 25, 2000

FROM: Mary Templeman, Code 5227

TO: **Code 6300 Dr Gubser**

CC: Tina Smallwood, Code 1221.1 *JR 10/30/00*

SUBJ: Review of NRL Reports

Dear Sir/Madam:

1. Please review NRL Reports FR-4467 and FR-4478 for:

☑   Possible Distribution Statement
☐   Possible Change in Classification

Thank you,

Mary Templeman
(202)767-3425
maryt@library.nrl.navy.mil

The subject report can be:

☒   Changed to Distribution A (Unlimited)
☐   Changed to Classification _____
☐   Other:

_____ 10/26/00
Signature   Date